Local moment, itinerancy and deviation from Fermi liquid behavior in Na_xCoO_2 for $0.71 \leq x \leq 0.84$

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Here we report the observation of Fermi surface (FS) pockets via the Shubnikov de Haas effect in Na_xCoO_2 for $x = 0.71$ and 0.84, respectively. Our observations indicate that the FS expected for each compound intersects their corresponding Brillouin zones, as defined by the previously reported superlattice structures, leading to small reconstructed FS pockets, but only if a precise number of holes per unit cell is *localized*. For $0.71 \leq x < 0.75$ the coexistence of itinerant carriers and localized $S = 1/2$ spins on a paramagnetic triangular superlattice leads at low temperatures to the observation of a deviation from standard Fermi-liquid behavior in the electrical transport and heat capacity properties, suggesting the formation of some kind of quantum spin-liquid ground state.

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The Na cobaltates Na_xCoO_2 are the subject of an intense interest due to i) an anomalously large thermoelectric response for $0.7 < x < 0.84$ [1, 2], ii) the discovery of superconductivity upon hydration for $x = 0.3$ [3], and iii) the overall complexity of their phase diagram as a function of x [4]. The thermoelectric response is particularly intriguing, since it is claimed to be associated with the presence of pronounced spin fluctuations [1] in the paramagnetic region of the phase diagram where the magnetic susceptibility displays Curie-Weiss (CW) behavior. CW response suggests the existence of localized magnetic moments in these metallic systems.

Initially it was thought that small Na concentration x corresponds to a lightly doped Mott insulator where correlation effects should be strong. However, it turns out that complicated magnetic order an CW behavior usually associated with strong correlations appear for $x \geq 0.5$. This is surprising because the $x = 1$ limit is a band insulator with all Co in the 3+ state with $S = 0$. Compounds with x slightly less than 1 should be thought of as hole doping of a band insulator, where correlation effects are weak because dilute carriers are moving in a featureless background. It has been suggested that the potential due to the ionized Na must play an important role [5] and calculations based on dynamical mean field theory show that by increasing the Na potential CW behavior appears [6]. Just as in doping of semiconductors, the ionized donor can trap carriers which form local moments once Coulomb repulsion between carriers is taken into account. This point of view received strong support from the recent discovery of well defined $\sqrt{13} \times \sqrt{13}$ and $\sqrt{12} \times \sqrt{12}$ superlattice structures for $x = 0.84$ and $x = 0.71$, respectively [7]. These superstructures can be explained if the Na ions form clusters of di-vacancies for $x = 0.84$ and alternating layers of tri-vacancies and quadra-vacancies for $x = 0.71$. The tendency towards vacancy clustering was first proposed by Roger *et al.*, [8] even though the detailed realization turns out to be different from their original proposal. In any event, vacancy clustering favors binding of a fraction of the carriers, because the clusters provide a stronger and more dilute binding potential than individual Na ions. This led Chou *et al.* [7] to propose a picture of co-existing local moments sitting on the superlattice and itinerant carriers for the doping range $x = 0.71$ to $x = 0.84$.

In order to find evidence for charge localization associated with the superlattice structures, we studied the size of their respective Fermi surfaces through electrical transport measurements at very high magnetic fields and very low temperatures to detect the Shubnikov the Haas (SdH) effect, previously seen in samples with lower values of x [9]. All crystals measured for this study, display typical resistivity ratios $\rho(300\ \mathrm{K})/\rho(0.6\ \mathrm{K})$ between 100 and 250 with residual resistivities ranging from 5 to 10 $\mu\Omega$ cm (data not shown here but data down to 4 K is reported in [10]). These values are nearly one order of magnitude lower than those reported previously by other groups, see for example [2, 11]. The exceptional quality of these crystals motivated us to explore the low temperature properties of their paramagnetic state. We performed a systematic study of the electronic and heat capacity properties as function of x, with x having values $(0.71 \pm 0.01) \leq x \leq (0.747 \pm 0.01)$ as determined via electron micro analysis (EPMA).

Single crystals of Na_xCoO_2 were grown using the floating-zone technique. Samples with different values of x were carefully produced via an electrochemical de-intercalation procedure, for details about sample growth see Ref. [10]. Resistivity measurements down to ^{3}He temperatures were performed using standard four-terminal techniques by using either a Physical Parameter Measurement System (PPMS) or a rotating sample

holder inserted into a ^{3}He cryostat coupled to magnetic fields up to $H = 45$ T provided by the hybrid magnet at the National High Magnetic Field Lab. Heat capacity measurements via the relaxation method down to $T = 350$ mK were also performed by using the PPMS.

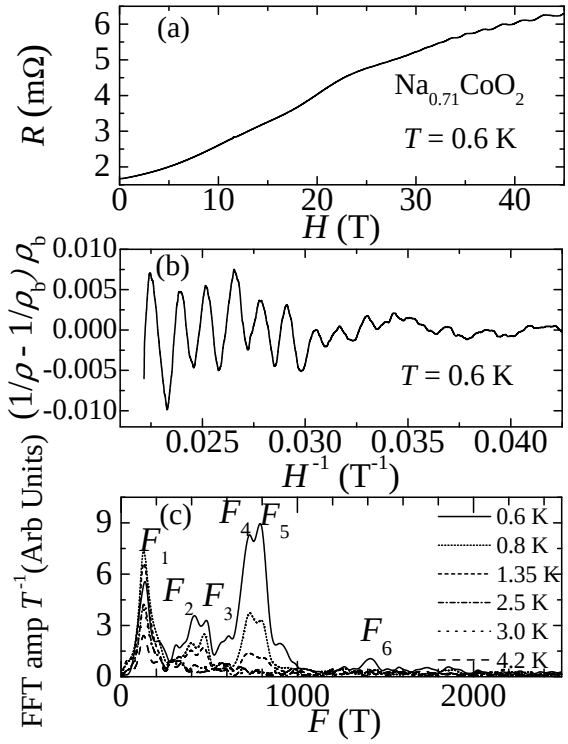

FIG. 1: (a) Resistance R as a function of field H for a $Na_{0.71}CoO_2$ single crystal at $T = 0.6$ K. (b) The SdH effect or the oscillatory component of R in (a) as a function of H^{-1}. (c) Amplitude of the fast fourier transform normalized by temperature T for several values of T. At least six frequencies are detected: $F_1 = 125$ T, $F_2 = 400$ T, $F_3 = 475$ T, $F_4 = 725$ T, $F_5 = 800$ T, and $F_6 = 1413$ T. The corresponding effective masses in units of free electron mass are: $\mu_1 = 1.2 \pm 0.9$, $\mu_2 = 6.9 \pm 1.6$, $\mu_3 = 4.4 \pm 0.4$, $\mu_4 = 12 \pm 1$, $\mu_5 = 10 \pm 1.4$, respectively.

Figure 1 (a) Shows a typical raw resistance trace for a Na_xCoO_2 single crystal with a Na concentration $x = 0.71 \pm 0.01$ as a function of field H applied along the inter-plane direction at a temperature $T = 0.6$ K. The oscillatory component seen at higher fields is the Shubnikov-de Haas (SdH) effect. We define the SdH signal as $(1/\rho - 1/\rho_b)\rho_b$ (where ρ is the resistivity and ρ_b is the background resistivity obtained from a polynomial fit) and it is displayed in Fig. 1(b) for the trace in (a). The fast Fourier transform (FFT) of the SdH signal is shown in Fig. 1 (c) for several temperatures. At least six peaks at well defined frequencies are observed in the FFT spectra which through Onsager relation $F = A(\hbar/2\pi e)$ correspond to cross sectional areas A of the Fermi surface perpendicular to the magnetic field. Two pairs F_2, F_3 and F_4, F_5 may originate from splitting by interlayer hopping. As in our previous reports [9] the observation of several Fermi surface pockets is at odds with all angle resolved photoemission studies (ARPES) [12, 13] which observe a single hole-like Fermi surface sheet associated with the A_{1g} band at the center of the hexagonal Brillouin zone. According to ARPES the area of this sheet scales with the effective carrier concentration $x' = 1 - 2A_{\rm FS}$, thus following the Luttinger theorem [12]. For $x = 0.75$, ARPES indicates a Fermi surface with an area corresponding to 12.5 % of the $A_{\rm FBZ}$ (area of the first Brillouin zone) when in reality all the pockets detect by us have an $A_{\rm FS} < 3$ % of $A_{\rm FBZ}$. (For example, $F_2 = 400$ T corresponds to $A_{\rm FS} \simeq 0.7$ % of $A_{\rm FBZ}$.)

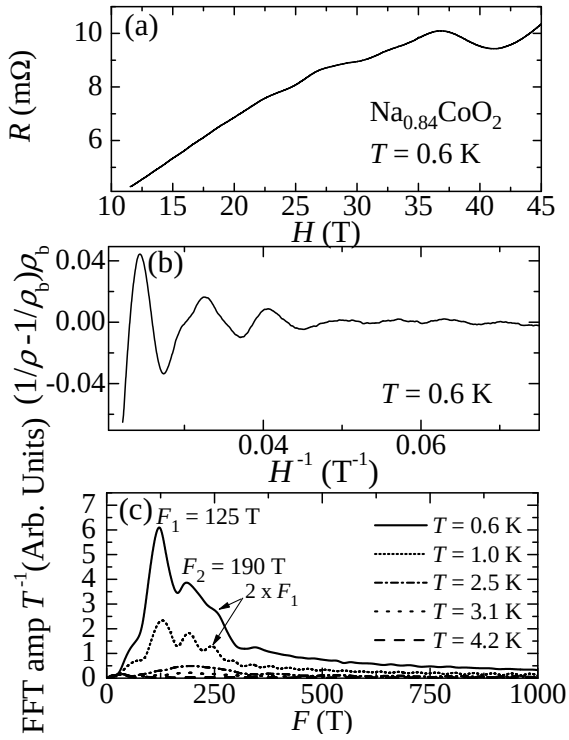

FIG. 2: (a) Resistance R as a function of field H for a $Na_{0.84}CoO_2$ single crystal at $T = 0.6K$. (b) The oscillatory component of R in (a) as a function of H^{-1}. (c) Amplitude of the fast fourier transform normalized by temperature T for several values of T. Two main frequencies are detected: $F_1 = 125$ T, $F_2 = 190$ T. The corresponding effective masses in units of free electron mass are: $\mu_1 = 7 \pm 1$, $\mu_2 = 5.6 \pm 0.3$, respectively.

Similar results are also obtained for $x = 0.84$. As in Fig. 1, in Fig. 2 (a) we show a typical resistance trace for a $Na_{0.84}CoO_2$ single crystal as a function of field at $T = 0.6$ K, in Fig. 2(b) the corresponding SdH signal, while Fig. 2 (c) shows the associated FFT spectrum. In contrast to $x = 0.71$, for $x = 0.84$ one sees only two peaks at very low frequencies, and related harmonics.

Fermi surface pockets are expected to result from the intersection of the Fermi surface with the new Brillouin zones induced by the Na superlattice structures

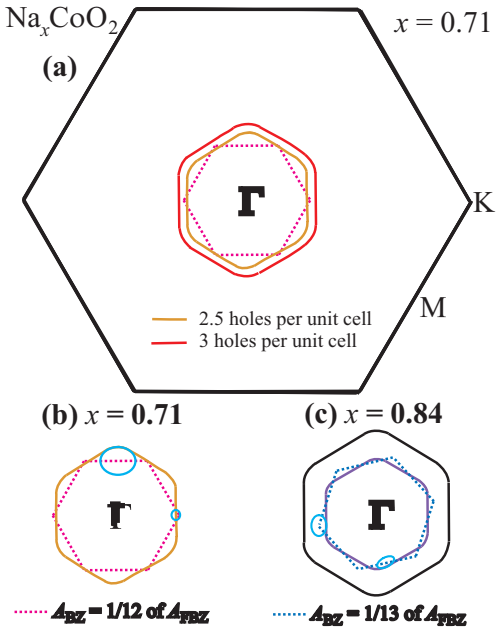

FIG. 3: (color online)(a) The Fermi surface for $x = 0.71 \simeq (1 - 3.5/12)$ within the hexagonal first Brillouin (FBZ) for 3 and 2.5 holes per reconstructed unit cell [7], respectively in red and in amber, assuming the absence of the ϵ'_g pockets. The dotted hexagon depicts the superlattice induced new Brillouin zone whose area is 1/12 of the area of the original FBZ. b) Fermi surface pockets (in clear blue) can result from the intersection between the new Brillouin zone and the Fermi surface depicted for 2.5 holes per reconstructed unit cell. c) Similarly, for $x = 0.84 \simeq (1 - 2/13)$ the superlattice induced new Brillouin zone (in blue), i.e., 1/13 of area of the original FBZ, and the spin polarized Fermi surfaces for 2 and 1 hole per unit formula, respectively in black and purple. Two Fermi surface pockets only result from the intersection of the new Brillouin zone and the originally depicted spin-polarized Fermi surface for 1 hole per reconstructed unit cell. Thus at least one hole per reconstructed unit cell is *localized*

seen for $x = 0.75$ and 0.84, namely $\sqrt{12}a \times \sqrt{12}a$ and $\sqrt{13}a \times \sqrt{13}a$, respectively [7]. In Figure 3 (a) we sketch the original (black line) and the superlattice induced (magenta line) hexagonal Brillouin zones for $x = 0.71$. Since $x = 0.71 \simeq 1 - 3.5/12$, one would naively expect that $A_{\rm FS}$ would be given by 3.5 holes per superlattice unit cell whose Brillouin zone has 1/12 of the area of the original Brillouin zone. But as can be seen in figures 3 (a) and (b), when one takes into account the spin degeneracy, only a Fermi surface whose area is given by at most 2.5 holes per superlattice induced formula unit will end up intersecting the new Brillouin zone leading to reconstructed Fermi surface pockets (clear blue lines) of very different cross-sectional areas. Here, following both ARPES [12, 13] and our previous results [9], we assumed the absence of the ϵ'_g pockets. Thus the FS pockets seen by us are a very strong indication that at least 1 hole per superlattice formula unit is in fact *localized* in $Na_{0.71}CoO_2$. Similarly, for $x = 0.84 \simeq 1 - 2/13$ one expects to have a Fermi surface whose area is given by 2 holes per unit cell which, in fact would intersect the superlattice induced Brillouin zone. But A-type antiferromagnetism, i.e., ferromagnetic planes coupled antiferromagnetically, has been reported for $x = 0.84$ [14] what de facto lifts the spin degeneracy in this system. Thus, as seen in Fig. 3 (c) a spin polarized Fermi surface, i.e., a half-metallic state, conformed by *one hole* per formula unit would intersect the new Brillouin zone leading to two small Fermi surface pockets as experimentally seen by us (Fig. 2 (c)). Consequently, also in this case we must have at least one localized hole per formula unit. Furthermore, in our sketch there are 2 pockets at the corners of the superlattice Brillouin zone, and 3 at its sides. Since the total FS area for both types of pockets should be equal, the respective ratio of their cross sectional areas is 3 to 2, as precisely seen in our experiment. Thus our results are clearly consistent with the presence of a single Na di-vacancy per superlattice unit cell [7].

The interplay between localization and itinerancy, which in most cases leads to rich new physical behavior, e.g. heavy-Fermions [15] and cuprate superconductors [16], is the central theme in strongly correlated electron physics. Here, the combination of localized but disordered $S = 1/2$ spins on a frustrated triangular superlattice which in the paramagnetic state interact with itinerant carriers, is expected to lead to unconventional physical response, particularly ar low temperatures where quantum spin fluctuations become predominant. In effect, as we show below, the low temperature properties of the paramagnetic state, i.e., $0.71 \leq x \leq 0.747$, are indeed quite anomalous. In Figure 4 (a) we present a contour plot displaying the evolution of the exponent of the resistivity $n = \partial \ln(\rho - \rho_0)/\partial \ln T$ for a $Na_{0.735}CoO_2$ single crystal as a function of field H for temperatures $T < 10$ K. As is clearly seen, n does not remain constant as function of temperature for any field value. Furthermore, at $H = 0$ it crossovers from two anomalous values, $n = 1$ to $n \sim 1.3$ at the lowest temperatures. This anomalous exponent is consistent with that found for the $x = 0.71$ samples [17] and disagrees with the exponent 2 found earlier in more disordered samples [11]. This value progressively increases with field until it reaches the conventional Fermi liquid value $n = 2$ for $H > 5$ T. This anomalous behavior in the resistivity if followed by a concomitant anomalous behavior in the heat capacity. In effect, in Fig. 4 (b) we plot the heat capacity normalized by temperature C/T for several concentrations $0.71 \leq x \leq 0.747$ at zero field. For $T < 10$ K, C/T crossovers from a constant value, the the electronic contribution in a Fermi liquid, at $x = 0.71$ to a nearly logarithmic dependence on temperature for $0.71 < x \leq 0.747$. C/T for $x = 0.71$ shows a remarkably large Sommerfeld coefficient $\gamma \simeq 52$ mJ/molK^2, which, to our knowledge is the largest value ever reported for the NaxCoO$_2$ series. This value is nearly 60 % higher

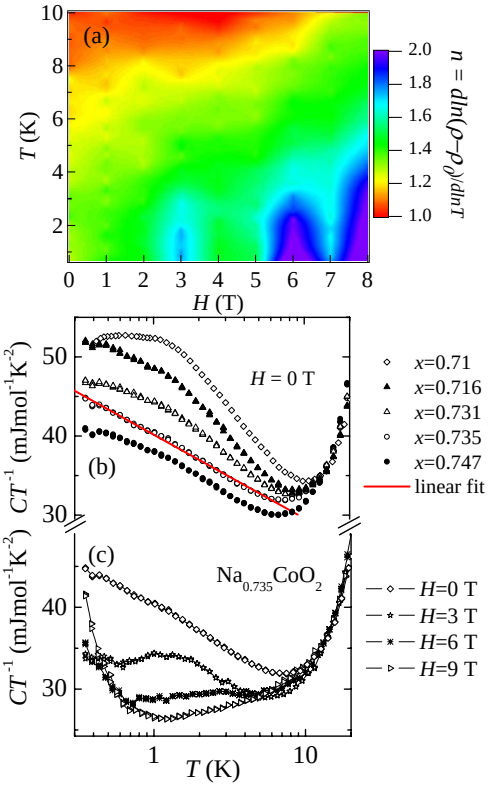

FIG. 4: (color online) (a) The evolution of the exponent of the resistivity $n = \partial \ln(\rho - \rho_0)/\partial \ln T$ as a function of field H for $0.6 \leq T \leq 10$ K for a $Na_{0.735}CoO_2$ single crystal. (b) Heat capacity normalized by temperature C/T as a function of T for several Na concentrations x in a semi-log scale. Straight line represents a linear fit to the $x = 0.735$ data over the temperature range $0.35 \leq T \leq 7$ K. (b) C/T as a function of T for $x = 0.735$ and for several values of the field H.

than the one previously reported for $x = 0.72$ [18] and it probably reflects the higher quality of our samples. Furthermore, as $x \rightarrow 0.75$ the nearly logarithmic dependence progressively spans over a larger range in temperatures and eventually, as can be seen for the $x = 0.735$ trace, the logarithmic dependence dominates C/T over a decade in T down to the lowest temperatures. The application of a magnetic field suppresses this anomalous behavior and a nearly constant but field dependent value of C/T is reached at lower temperatures prior to an upturn at the lowest temperatures which results from the Co nuclear Schottky term [19], see Fig. 4(c).

In summary, deviation from standard Fermi-liquid behavior is observed in the paramagnetic state of Na_xCoO_2 as $x \rightarrow 0.75$, and as a result of the interplay between itinerancy and localized $S = 1/2$ moments on a triangular superlattice. The upturn in the low temperature specific heat and the anomalous scattering in the resistivity both point to the existence of a novel kind of low energy excitations. That these excitations appear to be suppressed by a magnetic field suggests that these are spin fluctuations. One suggestion [7] is that the local moments form a spin liquid state [20] which co-exists with itinerant electrons. While our data does not allow us to draw any firm conclusion on the origin of the anomalous behavior, it is clear that the cobaltates offer a new window into possible novel ground states in a system with coupled local moments and itinerancy.

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